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Energy transfer in nanostructured oligothiophene inclusion compounds

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Abstract

Resonant energy transfers from terthiophene (T3) to quinquethiophene (T5) oligomers embedded in the nano-channels of perhydrotriphenylene (PHTP) crystals are studied by cw and femtosecond spectroscopy. The stringent geometry imposed by the host results in a very peculiar supramolecular organization of the guest molecules consisting of parallel linear arrays of chromophores. This provides a unique opportunity to make a quantitative analysis of the energy transfer phenomena and in particular to distinguish between heterotransfers and homotransfers. The experimental data fitted by a suitable theoretical analysis indicate that homotransfers become important in the long time dynamics and that the heterotransfer rate is satisfactorily described by the analytical solution obtained by assuming a continuous intermolecular spacing. © 2001 Elsevier Science B.V. All rights reserved

1. Introduction

Organic semiconductors are molecular materials formed by assemblies of molecules held together by weak Van der Waals forces, which implies that the properties of the solids are directly governed by those of the individual molecules which form the elemental bricks of the material and also by the way these bricks are spatially ordered. Recently much interest has been placed on supramolecular architectures – obtained by spontaneous self assembly or by layer by layer growth –

which realize controlled spatial organization of molecules. Fabrication of ordered arrays of conjugated molecules can also be obtained by their incorporation in host systems capable of forming nanochannels of suitable dimensions for containing the desired active molecules [1,2]. This approach has attracted considerable interest since it demonstrates the possibility to manifest macroscopic physical properties based on embedded microscopic structures. The potentiality of these host–guest systems is clear in the field of non-linear optics as parallel arrays of polar molecules exhibiting a macroscopic polarization (and therefore a macroscopic second-order response) can be fabricated [3].

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Energy transfer (ET) in organic semiconductors has been used to funnel the excitation produced by photon absorption onto properly chosen dopant which acts as the emitting species. By this process the energy is transported (spatially) and converted (energetically) by the following sequence: absorption of energy from a chromophore present in the system (indicated hereafter with D, donor); excitation transfer to another chromophore (A, acceptor); emission of radiation by the latter [4]. Energy transfer can also take place within the same molecular species (the D molecules), thus producing a fast migration of the excitation throughout the crystal [2,5]. Organic lasers [6] based on both fluorescent and phosphorescent dopants have been fabricated using this cascade process with the advantage of reducing unwanted absorption loss [7–9]. Even though long-range energy transfer phenomena based on dipolar interaction have been known and studied for many years, the precise interaction geometry on which individual $D \rightarrow A$ transfers depend, is often not known thus preventing a quantitative description of the process.

In this Letter we report on the studies of energy transfer in terthiophene (T3), donor, doped by quinquethiophene (T5), acceptor, organized in a nanostructured template (perhydrotriphenylene, PHTP) which allows a precise control of the interaction geometry. The role of the host is to provide the desired geometry to the supramolecular assembly, to stabilize the incorporated species and to prevent their aggregation even at the high concentrations of active molecules supported by the host structure. We address the following basic issues:

1. A quantitative comprehension of ET in doped active gain media is often prevented by the presence of different transfer phenomena, e.g., short-range hopping processes and long-range dipole–dipole interaction [10–12]. In fact, in standard systems (polymer blends, dye doped polymers and crystals), homotransfers can occur through two processes; (i) temperature dependent short-range hopping processes, whose rate is proportional to the overlap between the π wavefunctions of neighboring molecules ($\approx e^{-cR}$); and (ii) temperature independent Foer-

ster-type resonant transfers, which decay as R^{-6} . In most systems these two processes are both effective and therefore complicate the analysis of the experimental data [13,14]. The host–guest system investigated in the present work provides the unique opportunity to better understand the role played by the long-range homotransfer processes among linear conjugated molecules since the peculiar disposition of the molecules in the channels of PHTP prevents the short-range hopping processes. It is worth stressing that a quantitative understanding, and thus a control, of homotransfer along the channel is important for a directional and, possibly fast, flow of energy [2,5].

2. In this inclusion compound the precise knowledge of the donor–acceptor distances allows a comparison between a numerical calculation of the ET rate based on individual transfer events with the widely used analytical expression of the transfer rate in which any spatial and geometrical correlations in the molecular disposition are neglected, as a continuous distribution of point-like dipoles is assumed [15]. Moreover, the relatively large intermolecular separation ensures that the point-like dipole approximation used in the Foerster theory holds well, as compared to standard acceptor-doped amorphous matrices, usually investigated in the literature [10,13,14,16,17].

We investigate the energy transfer kinetics by means of cw and femtosecond photoluminescence spectroscopy, and analyze the experimental data by considering both the D–A and the D–D contributions to the Foerster resonant transfer from the D to A species. The present investigation shows that homotransfer becomes important and largely speeds up the energy transfer rate for delays longer than the characteristic transfer time between nearest donors. Then we show the comparison between the numerical calculations, which account for the exact distribution of the molecules in our matrix, and the analytical Foerster's expression of heterotransfer. We find that the analytical results describe the heterotransfer with good accuracy. In particular, although the analytical model allows for ultrafast D–A transfers at distances shorter than those available in our system,

this contribution to the energy transfer process is negligible.

2. Experimental

Oligothiophenes (T_n) inclusion and co-inclusion compounds are obtained from mixtures of T_n and PHTP ($\approx 1/10$)_w solutions by slow evaporation, as described elsewhere [18,19]. Co-inclusion of T5:T3 mixtures were obtained with different molar ratios $x = 0.002, 0.006, 0.015$ of T5/T3.

Cw measurements are performed by exciting with a monochromated Xe lamp with a SPEX spectrometer equipped with a cooled CCD detector. Time resolved measurements are performed by exciting with the second harmonic of a mode locked Ti:Sapphire with typical pulse width of 100 fs tuned at 810 nm. The PL signal was temporally analyzed by using non-linear optical gates allowing for a time resolution of 200 fs [20], and a Hamamatsu optical sampling oscilloscope with 20 ps time resolution.

3. Nanostructured oligothiophene inclusion compound

In the inclusion compound studied here, T3 and T5 molecules are located in the parallel nano-channels (whose distance is about 14 Å) formed by the host crystal PHTP (see Fig. 1), which is optically transparent in the visible region, therefore allowing transmission measurements of the included molecules [18]. The peculiarities of these oligothiophene inclusion compounds, with respect to the standard materials (as blends or crystals) are the following:

1. Chromophore aggregation is prevented since the channel/molecule dimensions prevent that the molecules glide past each other. This complete molecular separation can be obtained, in standard host–guest systems (e.g. blends), only for extremely low chromophore concentrations. The obtained molecular separation suppresses the very effective non-radiative decay channels induced by H-aggregation effects [21], even for the quite high chromophore concentrations

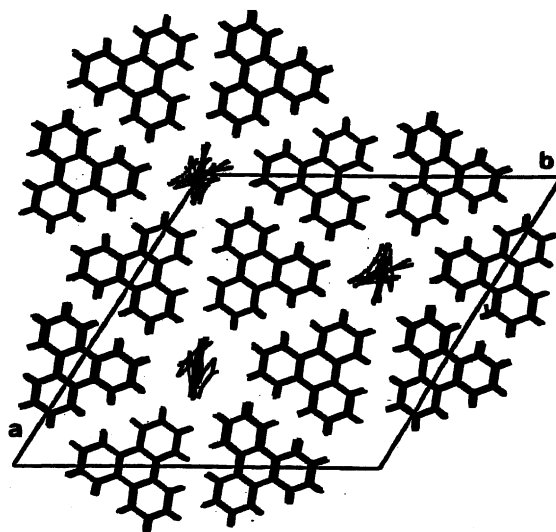


Fig. 1. Schematic structure of the T_n PHTP crystal, top view showing three channels.

used. For this reason, in the inclusion compound oligothiophenes become efficient emitters [18].

2. Fixed inter-channel distances (14 Å) give known inter-chromophore distances that, as described below, are in the range for which ET processes can take place.
3. The chromophore dipoles are oriented along the nanochannel axis. This provides the optimal relative orientation of the dipoles for efficient ET processes.
4. In this system temperature-dependent hopping processes can be neglected because of the large interchannel separation and of the head to tail arrangement of the molecules within the channel, which does not produce an appreciable intermolecular overlap of the electron wavefunctions.

4. Experimental results

In Fig. 2 the optical absorption and PL spectra of the D and A species (T3 and T5, respectively) are shown for the inclusion compounds. The spectral overlap between the absorption spectrum of T5 and the emission spectrum of T3 is quite

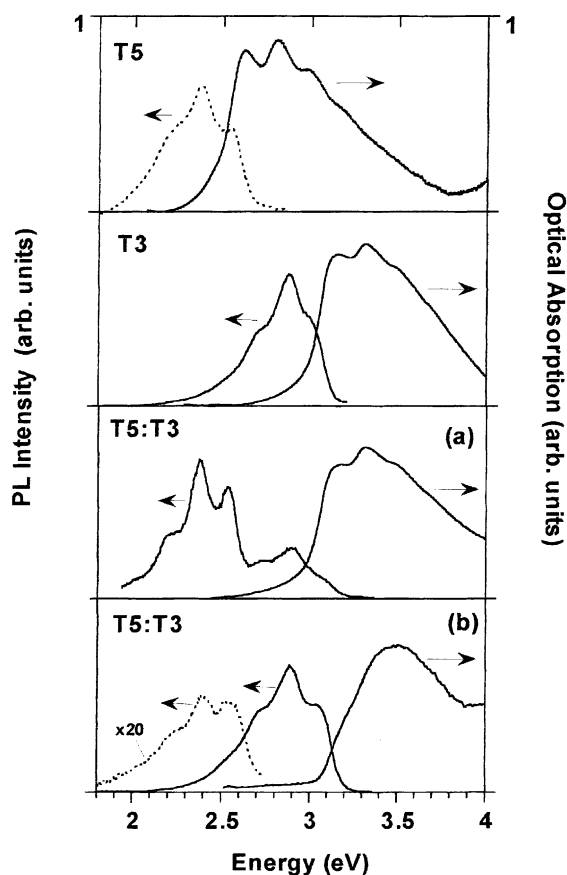


Fig. 2. Optical absorption and PL of T3 and T5 inclusion compounds dispersed in KBr; T5:T3 co-inclusion compound ($x=0.006$) in the solid state (a) and dissolved in solution (b). The PL spectra are obtained by exciting at 3.44 eV (solid lines) and 2.88 eV (dotted line), room temperature.

large so that an efficient D–A energy transfer via dipole–dipole coupling can be expected for the co-inclusion of these molecules in PHTP. In Fig. 2 the absorption and PL of the T5:T3 co-inclusion compound ($x=0.006$) crystals are shown. Both the emissions from T3 and T5 are observed in the PHTP crystal by exciting within the T3 absorption, while when the crystal is dissolved in diluted (about 10^{-4} M) THF solution, emission from T5 is not detected due to the increased D–A distances. The relative intensity of the PL of the two molecules in the PHTP crystal does not appreciably change with temperature or with the excitation wavelength. The spectral shape and position of the

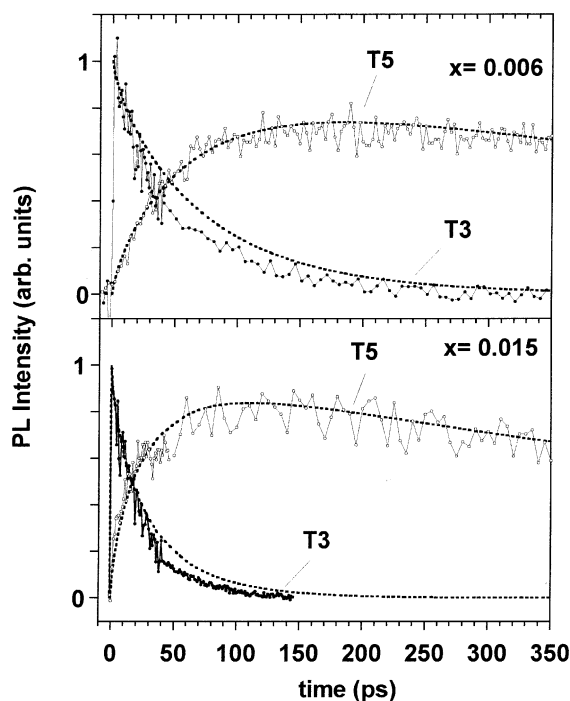


Fig. 3. PL transients of T3 and T5 for $x=0.006$ and $x=0.015$. Numerical simulations (dotted lines) following the model described in the text from Eq. (6). The PL data for times longer than 40 ps have been recorded using a streak camera.

PL of the inclusion compounds are the same as in solution, while the absorption spectra are red shifted. This is in agreement with the fact that, at room temperature, in solution the ground state conformation of the thiophene oligomers is distorted, and optical excitation induces a planarization of the molecule [22], while the ground state conformation of the molecules embedded into the PHTP crystal is quasi planar [23].

In Fig. 3 the time resolved photoluminescence of T3 and T5 are reported for T5:T3 co-inclusion compounds with increasing T5 concentration ($x=0.006$ and $x=0.015$). The decay time of the T3 emission and the rise time of the T5 emission become shorter for increasing concentration of T5.

5. Discussion

The observation of a rise time in the T5 PL of the co-inclusion compound demonstrates that the

T5 excited state is not directly populated by photon absorption, but its population, and hence PL emission, originates from an energy transfer from the excited T3 molecules. The fast decay time observed for the T3 molecules, and its dependence on the T5 concentration, is consistent with the presence of a non-radiative quenching of the T3 emission due to the ET to T5. In the following we analyze the experimental results in term of long-range energy transfer among the oligomers in the PHTP matrix.

According to Foerster's theory ET can only occur if a spectral overlap between the donor emission and the acceptor absorption takes place (resonance conditions) and if a suitable interaction between both systems exists. The transfer rate, describing the energy transfer due to the interaction between the transition moments of the A and D species, separated by a distance R , can be expressed by [24]

$$k_{\text{DA}} = \frac{1}{\tau_{\text{D}}} \left(\frac{R_0}{R} \right)^6 = \frac{9000 \ln 10 \Gamma^2 \eta_{\text{D}}}{128 \pi^5 n^4 N \tau_{\text{D}} R^6} \int_0^\infty \frac{F_{\text{D}}(\omega) \varepsilon_{\text{A}}(\omega) d\omega}{\omega^4}, \quad (1)$$

where η_{D} is the quantum yield of the donor in the absence of the acceptor, n is the refractive index of the medium, N is the Avogadro's number, τ_{D} is the lifetime of the donor in the absence of the acceptor, Γ^2 is a factor describing the relative orientation in the space of the transition dipoles of the donor and acceptor [24], the integral represents the spectral overlap between the (normalized) emission spectrum $F_{\text{D}}(\omega)$ of the D species and the extinction coefficient $\varepsilon_{\text{A}}(\omega)$ of the A species, and R_0 is the Foerster distance, for which the donor natural decay and the donor–acceptor transfer have the same probability.

Two factors affect therefore the ET rate: (i) the spectral matching conditions between the D and A molecular species; (ii) the intermolecular distance and the relative orientation of the D and A molecular dipoles. In isotropic samples, the orientational factor $\Gamma^2 = 2/3$ of dipoles randomized by rotational diffusion in solution, is usually assumed [4], however, in our case the relative orientations of the donor and acceptor dipoles are fixed and

dictated by the geometry of the channels and the geometrical factor assumes the simple form

$$\Gamma_{ij} = [3 \cos^2 \theta_{ij} - 1], \quad (2)$$

where θ_{ij} is the angle between the molecular dipoles and the distance R_{ij} between the baricenters of molecules at sites i and j . In the case of head to tail arrangement of the transition dipoles ($\theta = 0$), such as those within the channels, $\Gamma^2 = 4$; while for parallel dipoles located in the same position of lateral channels ($\theta = \pi/2$), $\Gamma^2 = 1$. In our case, namely for a static random distributions of molecules possessing parallel dipole orientation, a value of $\Gamma^2 = 0.593$ was inferred [25].

By assuming the values for the acceptor (T5) extinction coefficient ε_{A} and the donor (T3) PL quantum efficiency η_{D} reported in the literature for the solutions [26,27], we obtain $R_0 = 33 \text{ \AA}$ from Eq. (1) for a statistical distributions of molecules with parallel dipole orientations ($\Gamma^2 = 0.593$). For ET processes taking place only within a channel (longitudinal transfers) the Foerster radius considerably increases ($R_0 = 45 \text{ \AA}$) while for the case of purely transverse inter-channel ET $R_0 = 36 \text{ \AA}$. The corresponding values for the donor–donor Foerster transfers, obtained from the spectral superposition of the donor (T3) absorption and emission (see Eq. (1)) are $R_0^{\text{DD}} = 22$ and 18 \AA for intra- and inter-channel donor–donor transfers, respectively.

These values are compatible with efficient ET occurring among the included molecules. By considering the intermolecular distances in the PHTP crystal, from Eq. (1) we can calculate the longitudinal and transverse transfer times among nearest neighbors D–A of 650 and 608 fs, respectively. Longer times are obtained for longitudinal and transverse transfer among D–D nearest neighbors of 11 and 43 ps, respectively. For the acceptor concentrations analyzed, these values indicate that the main transfer processes occur among T3 and T5, even though the occurrence of slower transfer processes among T3 (mainly longitudinal) might increase the T3–T5 transfer rate at long times. Some of the possible ET steps occurring in the inclusion compound are schematically depicted in Fig. 4.

By assuming that the D and A molecules are randomly located within the channels (with the

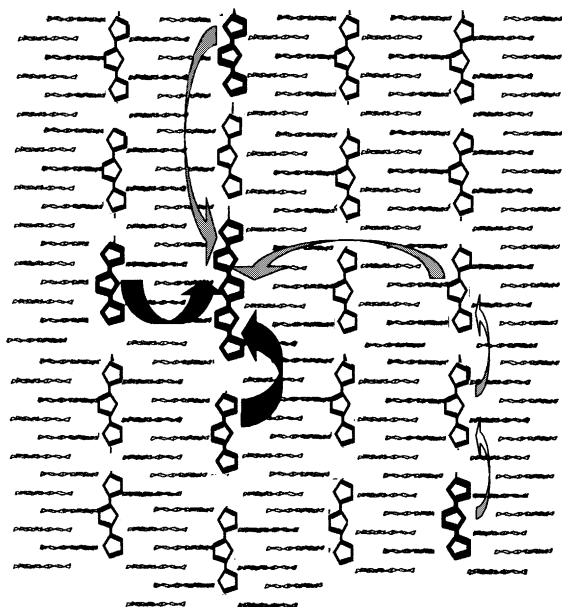


Fig. 4. Schematic lateral view of the structure of the T5:T3 PHTP crystal with a sketch of some possible individual transfer processes represented by arrows.

constraint of the concentration ratio x), the rate equations for the donor and acceptor populations can be written as [28]

$$\begin{aligned}\frac{dn_D}{dt} &= -\frac{n_D}{\tau_D} - kn_D, \\ \frac{dn_A}{dt} &= -\frac{n_A}{\tau_A} + kn_A,\end{aligned}\quad (3)$$

where the rate constant k is the sum of the transfer rates for the excitation, which at time t is at the site j , towards all the N_A acceptor molecules:

$$k^{DA} = \frac{1}{\tau_D} \sum_{i=1}^{N_A} \Gamma_{ij}^2 \left(\frac{R_0}{R_{ij}} \right)^6, \quad (4)$$

where R_{ij} is the distance between excited D species at the site j and the acceptors. In the case in which donor–donor transfer is neglected, k^{DA} does not depend on time. Conversely, if donor–donor transfer is considered, the site j where the excitation is located changes during time, and so k^{DA} does. The probability that the donor excitation is transferred from site j to site l is equal to $k_{jl}^{DD} \Delta t$, where k_{jl}^{DD} is given by

$$k_{jl}^{DD} = \frac{1}{\tau_D} \Gamma_{jl}^2 \left(\frac{R_0^{DD}}{R_{jl}} \right)^6. \quad (5)$$

For the donor–donor transfer we only consider nearest-neighbors jumps within the channels, which are by far the fastest ones (we have found that the inclusion of 3D donor–donor transfers gives the same dynamics). In order to evaluate whether a jump will occur or not, and, in the case it occurs, to which site the donor excitation will be transferred, we use the following procedure. We generate a random number p between 0 and 1. The jump will occur only if $0 < p < 2k_{jj+1}^{DD} \Delta t$ ($k_{jj+1}^{DD} = k_{jj-1}^{DD}$). If p is less than $k_{jj+1}^{DD} \Delta t$, the donor will jump to the site $j+1$; if $k_{jj+1}^{DD} \Delta t < p < 2k_{jj+1}^{DD} \Delta t$, the donor will jump to the site $j-1$. In this way, we can calculate the position of the donor excitation at any time, and the value of k^{DA} as well. At this point, $n_{A(D)}$ can be numerically calculated as follows:

$$\begin{aligned}n_A(t + \Delta t) &= n_A(t) + \frac{dn_A}{dt} \Delta t, \\ n_D(t + \Delta t) &= n_D(t) + \frac{dn_D}{dt} \Delta t,\end{aligned}\quad (6)$$

where $dn_{A(D)}/dt$ are calculated from Eq. (3). Finally, we obtain the average $\langle n_{A(D)}(t) \rangle$ for different random configurations of the acceptor and donor molecules in the host crystal. Since oligothiophenes completely fill the PHTP nanochannels, which form an hexagonal lattice [23], we have assumed intrachannel and interchannel distances between molecule baricenters of 18 and 14 Å, respectively, for D–A transfers, and 14 Å for both D–D transfers. The calculated PL temporal dynamics for both the T3 and T5 are shown in Fig. 3 and compared to the experimental time resolved data. We stress that all the inputs of the model ($R_0, \tau_D = 170$ ps, $\tau_A = 880$ ps) are experimentally available [27] and no fitting parameters are used in the numerical simulations.

In order to establish the effect of donor–donor transfer on the PL dynamics, we have applied the same procedure to the simpler case of only donor–acceptor transfers. As it can be seen in Fig. 5, by neglecting the contribution of T3–T3 transfers, the short time (< 20 ps) decay is not influenced, but for longer times a slower decay is obtained.

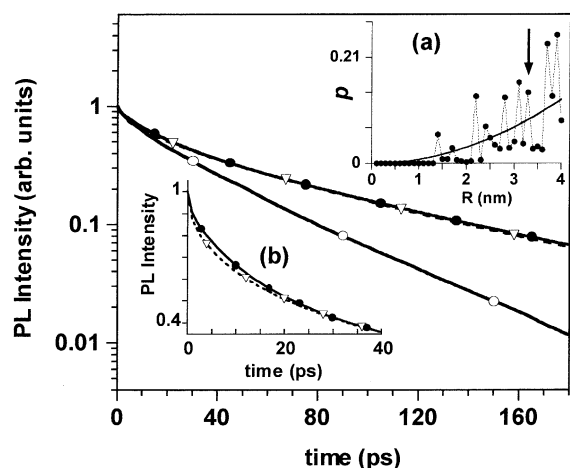


Fig. 5. Numerical simulations of T3 PL transients for $x = 0.015$ from Eq. (6) by including (open circles) and neglecting (solid circles) the D–D homotransfer; and the analytical solution (dotted line, triangles) from Eq. (7) for parallel dipoles orientations. In the inset (a), the probability p of finding an acceptor at a distance R from the excited donor is shown for $x = 0.015$, both for the continuous (solid line) and the discrete distributions (points). The arrow indicates the Foerster radius position. In the inset (b) an enlargement of the heterotransfer short time decays is shown from Eqs. (6) and (7).

This indicates that for this model system, *where short-range D–D hopping processes cannot occur*, resonant energy homotransfer processes can be neglected only at early times, but they must be taken into account in order to correctly describe the longer time dynamics. In fact for delays longer than the characteristic transfer time between nearest donors (11 ps, see previous discussion), resonant D–D transfers can effectively reduce the D–A distances thus increasing the D–A transfer rate.

We now compare the donor decay dynamics obtained by considering the effective discrete distribution of molecules in the crystal, with the analytical solution of the D–A transfer rates obtained by assuming a continuous distributions of point-like molecules, generally used to fit experimental data in doped polymer systems [10,13,16]. The two distributions are shown in the inset (a) of Fig. 5. The probability p of finding an acceptor at a distance $R + dR$ ($dR = 1$ Å) from the excited donor is shown for the acceptor concentration $x = 0.015$, both for the continuous and the

discrete distributions. The former one allows for ultrafast D–A transfers for distances below 14 Å (the transfer rate depends on the sixth-power of the intermolecular distance), which cannot occur in the inclusion compound studied here. The analytical expression describing the decay of the donor PL due to D–A transfer (neglecting the D–D transfers) in continuous homogeneous distributions of point-like molecules, can be written as [15]

$$n_D(t) \approx N_D e^{-t/\tau_D} e^{-2\gamma\sqrt{t/\tau_D}}, \quad (7)$$

where γ , which depends on the ratio between the acceptor and the critical concentrations, can be written for our system as $\gamma = 4(\pi/3)^{3/2}(R_0/d)^3x$, where d is the interchannel distance. In Fig. 5, the analytical decays described by Eq. (7) for statistical distribution of molecules possessing parallel dipole orientations ($R^2 = 0.593$) are shown. As it can be seen, the analytical solution of the Foerster ET gives a D decay similar to the one obtained with the numerical analysis, neglecting the D–D contribution. A slightly faster initial decay of the donor population (see inset (b) of Fig. 5) is predicted by the analytical solution which allows for D–A transfers at intermolecular distances below 14 Å, which are not compatible with the chromophore disposition in the inclusion compound. However, the probability that an excitation undergoes such fast D–A transfers is small (see inset (a)) and therefore, for most purposes, the analytical Eq. (7) represents a very good approximation for the D–A kinetics. This can be rationalized by considering that the transfer probability for distances smaller than the chromophore dimension (for which the point dipole approximation should not hold) is negligible.

6. Conclusion

We have investigated the energy transfer from T3 to T5 molecules embedded in the parallel nanochannels of PHTP. In this compound Foerster energy transfer takes place in a controlled geometrical arrangement of the donor and acceptor species. Heterotransfers (T3–T5) and homotransfers (T3–T3) provide a good quantitative

description of the decay and build up, respectively, of the donor and acceptor populations as determined by time-resolved photoluminescence experiments. Even though the supramolecular organization of the chromophore in the IC implies discrete intermolecular transfer distances, we have shown that the analytical approach usually employed, which averages over a continuous distribution of transfer distances, deviates only slightly from the more rigorous numerical approach based on the precise knowledge of the interaction geometry.

Due to the smaller spectral overlap among donor absorption and emission, the contribution of D–D resonant transfers in the D quenching dynamics is negligible at times shorter than 20 ps. Its contribution must be however included in the D decay dynamics to account for the faster quenching experimentally observed at longer times. This demonstrates that, even in absence of short-range hopping processes, resonant homotransfer contribution can sensitively increase the long time transfer rate. Finally, in order to get a faster directional flow of energy, the present study suggests that D–D distances should be sensitively reduced, e.g., by choosing shorter molecules; or, as suggested by Eq. (1), by increasing the spectral overlap between absorption and emission of the donors, a requirement that can be fulfilled in molecules with smaller electron–vibrational coupling.

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